PB85-231900

Permeability of Polymeric Membrane Lining Materials for Waste Management Facilities

Matrecon, Inc., Oakland, CA

Prepared for

Environmental Protection Agency, Cincinnati, OH

May 85

U.S. Department of Commerce
National Technical Information Service
NTIS

TECHNICAL REPORT DATA
(Please read Instructions on the reverse before completir

1. REPORT NO. EPA/600/D-85/143	2.
3. F PB85-231900	
4. TITLE AND SUBTITLE Permeability of Polymeric Membrane Lining Materials for Waste Management Facilities	5. REPORT DATE May 1985
	6. PERFORMING ORGANIZATION CODE
7. AUTHOR(S) H.E. Haxo, Jr., J.A. Miedema, and N.A. Nelson	8. PERFORMING ORGANIZATION REPORT NO.
9. PERFORMING ORGANIZATION NAME AND ADDRESS Matrecon Inc. Oakland, CA	10. PROGRAM ELEMENT NO.
	11. CONTRACT/GRANT NO.
12. SPONSORING AGENCY NAME AND ADDRESS Water Engineering Research Laboratory-Cincinnati, OH Office of Research and Development U.S. Environmental Protection Agency Cincinnati, OH 45268	13. TYPE OF REPORT AND PERIOD COVERED Journal Article
	14. SPONSORING AGENCY CODE EPA/600/14

15. SUPPLEMENTARY NOTES R. Landreth, (513) 684-7836
In: Elastomerics, 117(5):29-36, 66, May 1985

16. ABSTRACT

This paper discusses the types of materials used in the manufacture of polymeric liners for waste management and the permeability of such liners. It also presents experimental permeability results for a range of commercial polymeric membranes to gases, water vapor, and solvent vapors. Current results of studies of the permeability characteristics of membranes as observed in pouch experiments are presented.

17. KEY WORDS AND DOCUMENT ANALYSIS

a. DESCRIPTORS	b. IDENTIFIERS/OPEN ENDED TERMS	c. COSATI Field/Group

REPRODUCED BY
NATIONAL TECHNICAL
INFORMATION SERVICE
U.S. DEPARTMENT OF COMMERCE
SPRINGFIELD, VA. 22161

18. DISTRIBUTION STATEMENT RELEASE TO PUBLIC	19. SECURITY CLASS *(This Report)* UNCLASSIFIED	21. NO. OF PAGES 11
	20. SECURITY CLASS *(This page)* UNCLASSIFIED	22. PRICE

EPA Form 2220-1 (Rev. 4-77) PREVIOUS EDITION IS OBSOLETE

NOTICE

This document has been reviewed in accordance with U.S. Environmental Protection Agency policy and approved for publication. Mention of trade names or commercial products does not constitute endorsement or recommendation for use.

EPA/600/D-85/143
May 1985

Permeability of Polymeric Membrane Lining Materials for Waste Management Facilities

Henry E. Haxo, Jr.
Jelmer A. Miedema
Nancy A. Nelson

Matrecon, Inc.
Oakland, CA

Because of their low permeability to gases, liquids, and vapors, flexible polymeric membranes offer a feasible approach to meeting the requirements of the EPA's regulations for the lining of waste storage, treatment, and disposal facilities to prevent migration into the groundwater of waste liquids and their constituents.

In the initial use of liners for waste disposal facilities, the primary purpose was to control the transmission of water and trace metals to the groundwater. To these species polymeric membranes have shown extremely low permeability. However, polymeric compositions are well known to be permeable to organic species *(9, 10)*, and differ greatly in magnitude, depending on the polymeric material and the permeating fluid or molecular species. The migration of organics, which is of great concern in groundwater protection, should be controlled by membrane liners which can also be used to control the movement of gases and organic vapors into the atmosphere from landfills and waste impoundments. From the standpoint of designing lined hazardous waste facilities, it is important to know the magnitude of the permeability of the polymeric membranes to different constituents and combinations and to know the driving forces that are involved so that transmission rates can be estimated.

This paper discusses the types of materials used in the manufacture of polymeric liners for waste management and the permeability of

Table I — Polymeric Materials Used in Liners

Polymer	Abbreviation	Type of Compound*	Thickness, mm	Fabric Reinforced
Butyl rubber	IIR	XL	0.9-2.3	Yes, no
Chlorinated polyethylene	CPE	TP	0.5-1.0	Yes, no
Chlorosulfonated polyethylene	CSPE	TP, XL	0.6-1.0	Yes, no
Elasticized polyolefin	ELPO	CX	0.8	No
Elasticized polyvinyl chloride	PVC-E	TP	0.8-0.9	Yes
Epichlorohydrin rubber	ECO	XL	1.67	Yes, no
Ethylene propylene rubber	EPDM	XL, TP	0.5-1.6	Yes, no
Neoprene	CR	XL	0.5-1.8	Yes, no
Nitrile rubber	NBR	XL	0.8	Yes
Polybutylene	PB	CX	0.8	No
Polyester elastomer	PEL	TP, CX	0.5-0.8	Yes, no
Polyethylene, low-density	LDPE	CX	0.3-0.8	No
low-density, linear	LLDPE	CX	0.5-2.0	No
high-density	HDPE	CX	0.5-3.1	No
Polyvinyl chloride	PVC	TP	0.5-0.9	Yes, no
Polyvinyl chloride - oil-resistant	PVC-OR	TP	0.8	No

*TP = Thermoplastic; CX = Partially crystalline; XL = Crosslinked.

Table II — Basic Compositions of Polymeric Membrane Liner Compounds

Component	Composition of compound type, parts by weight		
	Crosslinked	Thermoplastic	Semicrystalline
Polymer or alloy	100	100	100
Oil or plasticizer	5-40	5-55	0.10
Fillers:			
Carbon black	5-40	5-40	2-5
Inorganics	5-40	5-40	...
Antidegradants	1-2	1-2	1
Crosslinking system:			
Inorganic system	5-9	•	...
Sulfur system	5-9	...	...

•An inorganic curing system that crosslinks over time is incorporated in CSPE liner compounds.

such liners. It also presents experimental results for a range of commercial polymeric membranes to gases, water vapor, and solvent vapors. Current results of studies of the permeability characteristics of membranes as observed in pouch experiments are presented.

Type Composition of Polymeric Membranes

Polymers used in the manufacture of lining materials include rubber and plastics differing in basic chemical composition and structure, solubility characteristics, chemical resistance, and the mode in which they deteriorate and ultimately fail. These polymers can be classified into four general types:

- Rubbers (elastomers) that are generally crosslinked.
- Thermoplastic elastomers that are not crosslinked but may contain some crystallinity.
- Plastics that are generally not crosslinked.
- Plastics that are thermoplastic and have a relatively high crystalline content, such as the polyethylenes.

Table I lists the types of polymers that are used in membranes. The polymers most frequently used in liners have been PVC, CSPE, CPE, IIR, EPDM, CR, and HDPE. The thickness of commercial polymeric membranes for liners ranges from 0.5 to 3.0 mm, with most in the 0.75 to 1.5 mm range.

Most polymeric membranes are based on single polymers, but blends of two or more polymers are being developed and used in liners. Also, different grades of a given type of polymer can be used. Generic classifications based on individual polymers have become increasingly difficult even though one polymer may predominate. All polymers are compounded with auxiliary ingredients which serve different purposes.

The basic compositions of the different types of compounds are shown in Table II. The crosslinked compositions are usually the most complex because they contain a crosslinking system. Thermoplastics, except for CSPE compounds, contain no curatives. Although supplied as thermoplastic CSPE liners contain crosslinking agents that allow the polymer to crosslink during service. Crystalline materials have the simplest composition and generally consist of the polymer, a small amount of carbon black for ultraviolet protection, and antidegradants.

Several of the auxiliary components of a formulation can be affected during service when they are either immersed in the liquid or exposed to the weather. Low molecular weight fractions in the original polymer or blend can be lost. The oils and plasticizers are potentially extractable and, in some cases, biodegradable; antidegradants can be extracted. Loss or change in any of these components can affect properties and durability of the compound.

Most of the polymeric membrane liners currently manufactured are thermoplastic. Even if the polymer in the crosslinked form is more chemically resistant (such as CPE and CSPE), it is generally supplied as a thermoplastic because it is easier to obtain reliable seams and to make repairs in the field. Thermoplastic polymers can be heat-sealed or seamed with a solvent or bodied solvent. Crystalline sheetings are generally seamed by thermal welding or fusion methods.

Membranes of all but the crystalline type compositions are available with fabric reinforcement to increase strength and thermal stability. The fabric constructions vary from thread counts of 6 x 6 to more than 20 x 20. As the thread count increases, the area between the threads that allows contact between the plies is reduced. The adhesion between plies is dependent upon this area and good "knitting" of the polymeric layers during manufacture. Good initial ply adhesion and its retention during service are important to prevent delamination.

Information on individual polymers and liners is presented in the EPA Technical resource document on liners*(7)*.

Transport Through Polymeric Membranes

In contrast to clay soils and various admixes which have been used as liners in waste management, polymeric membrane liners are nonporous. With porous materials the flow of liquids containing dissolved constituents is through the pores and the principal driving force is the hydraulic gradient. For nonporous membranes, the transport of a permeating fluid, be it gas, liquid, or vapor, depends on the solubility of the constituent in the membrane and its diffusibility in the membrane. This transport proceeds essentially in three steps:

- Dissolution of the fluid or constituent into the membrane. *(Step No. 1)*
- Diffusion of the dissolved fluid through the membrane. *(Step No. 2)*
- Evaporation or dissolution of

the fluid on the downstream side of the membrane. *(Step No. 3)*

Step No. 1 depends upon the solubility of the fluid in the membrane and relative "activity" of the fluid on both sides of the interface. The diffusion through the membrane in Step No. 2 involves a variety of parameters which include the molecular size of the permeating fluid and various characteristics of the membrane compound. e.g. presence of fillers, crystalline zones, plasticizers, crosslinks, etc. Step No. 3 is similar to the first step and depends upon the relative "activity" of individual constituents on both sides of the interface at the downstream liner surface.

The major driving force for the movement of a given constituent through a membrane is its "activity" gradient across that membrane. Each constituent in a gaseous or liquid mixture tends to move independently from a higher to a lower "activity." In many situations the concentraction or vapor pressure is equivalent to the "activity."

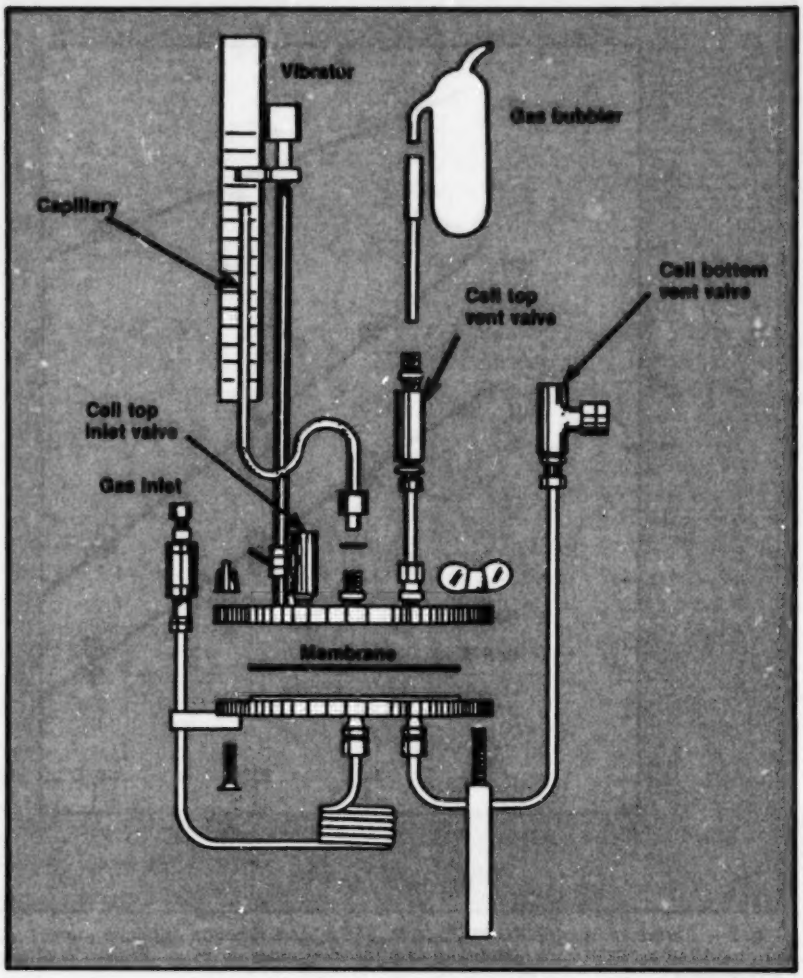

Fig. 1 — Gas permeability apparatus in ASTM D1434, Procedure V - Volumetric (1).

Gas Permeability

Permeability to gases, particularly methane, is an important factor in the use of polymeric lining materials for the control of gas migration in a variety of engineering applications. These include such uses as covers and curtain walls to control movement of methane from landfills and as barriers to prevent entrance of methane into buildings and other structures near municipal solid waste (MSW) landfills.

The permeability of membrane liner materials to three gases of interest in land disposal facilities was determined by ASTM D1434, Procedure V - Volumetric*(1)*. In this procedure a specimen of the liner is clamped into a stainless steel cell to form a barrier to gas flow through the cell. All air is flushed from the system with the test gas and then one side of the cell is maintained at a positive pressure while the other remains at atmospheric pressure. A capillary mounted on the atmospheric pressure side of the cell is used to monitor the volume of gas slowly diffusing through the liner. The test apparatus is shown in Fig. 1.

In determining permeability, both the system pressure and cell temperature must be maintained as constant values throughout the test. Reproducible data cannot be obtained until the test gas, cell, and membrane are at thermal equilibrium and the membrane has reached equilibrium in its absorption of the test gas. When these conditions are met, the passage of test gas through the membrane will reach a steady state rate and the permeability determination is made.

Data collection consists of tabulating the linear displacement of the liquid meniscus within the capillary versus time. These data can be reduced to a displacement rate using a linear regression routine and further reduced to the gas transmission rate (GTR) in terms of gas volume/area x time x Δ pressure if the capillary diameter, specimen surface area, and applied pressure differential are recorded. Determination of the gas transmission rate at two or more temperatures allows the calculation of an activation energy (E_d) and of a preexponential factor (log GTR_o) for the transmission process. Knowledge of these two parameters for a given liner-gas combination makes possible the calculation of the gas transmission rate at any temperature.

Figure 2 illustrates the relation between temperature and transmission rates of carbon dioxide, nitrogen, and methane through an elasticized polyolefin (ELPO) membrane number 36. This relationship is roughly linear over a moderate temperature range and may be expressed by the following equation:

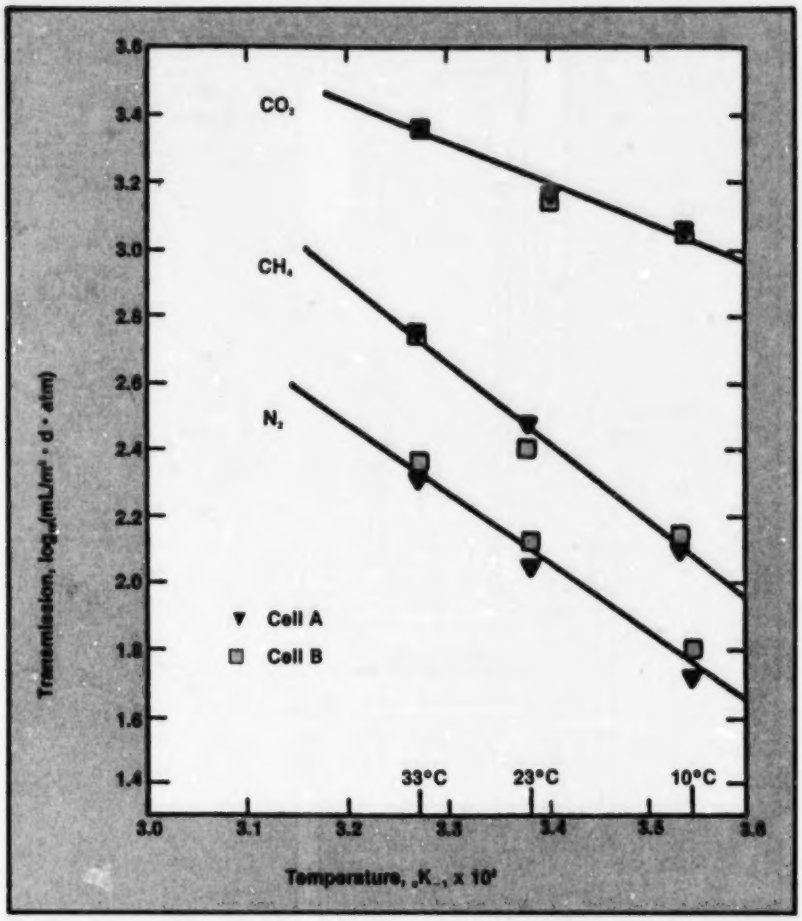

Fig. 2 — Permeability of ELPO to CO_2, CH_4, and N_2 as a function of temperature. Data are reported as GTR for a membrane of 0.158 mm under pressure difference of one atmosphere.

$\log GTR = \log GTR_o - E_d/RT$

where

$\log GTR$ = $\log_{10}$ of the transmission rate at T in mL (STP)/$m^2 \cdot d \cdot atm$

$\log GTR_o$ = the preexponential factor (y-intercept)

E_d = activation energy in calories/mole = − slope × R

R = gas constant = 1.987 cal/mole·°K

T = temperature in degrees Kelvin (°C + 273.16)

Table III — Temperature Dependence of the Permeability of ELPO Membrane[a] to Carbon Dioxide

Cell	Temperature, °C	$(T°K)^{-1}$	Gas transmission rate: mL (STP)/$m^2 \cdot d \cdot atm$	Gas transmission rate: Log_{10} GTR	Gas permeability coefficient: Barrer[b]	Gas permeability coefficient: Log_{10} barrers
A	10	3.531×10^{-3}	1120	3.0492	9.90	0.996
A	23.1	3.376×10^{-3}	1410	3.1492	12.40	1.09
A	33.0	3.266×10^{-3}	2290	3.3598	20.20	1.31
B	10	3.531×10^{-3}	1150	3.0607	10.10	1.00
B	23.1	3.376×10^{-3}	1490	3.1732	13.10	1.12
B	33.0	3.266×10^{-3}	2330	3.3674	20.50	1.31

[a]Liner number 36; thickness used in calculation of gas permeability coefficient for specimen in Cell A is 0.580 mm, and for specimen in Cell B is 0.578 mm.
[b]One barrer = 10^{-10} mL (STP)·cm/$cm^2 \cdot s \cdot$ cm Hg.

The data for CO_2 used in Figure 2 are tabulated in Table III. Reduction by linear regression yields a slope of -1.1612×10^3, a y-intercept of 7.1384, and a correlation coefficient of −0.97949. The activation energy and preexponential factors are calculated as follows:

preexponential factor =

$\log GTR_o$ = y-intercept = 7.1384

Activation energy =

$E_d = -\text{slope} \times R$

$= 1.1612 \times 10^3 \times 1.987$

$= 2.307 \times 10^3$

The rate of permeation at 0°C can then readily be determined:

$\log GTR = \log GTR_o - E_d/RT$

$\log GTR = 7.1384 - (2.307 \times 10^3)/(1.987 \times (0 + 273.16))$

$\log GTR = 2.8880$

$GTR = 773$ mL (STP)/$m^2 \cdot d \cdot atm$ for CO_2 through the ELPO membrane at 0°C.

Data for the permeability at 23°C of a series of polymeric membrane liners to carbon dioxide, methane, and nitrogen are presented in Table IV on both the basis of gas transmission rates which are indicative of liner performances, and on the basis of permeability coefficients which are material properties and reflect the permeabilities of the liner compounds. The conversion (ASTM D1434) of gas transmission rate (GTR) in mL (STP)/$m^2 \cdot d \cdot atm$ to permeability coefficient ($\bar{P}$) in barrers [10^{-10} mL (STP)·cm/$cm^2 \cdot s \cdot$ cm Hg] is:

$\bar{P}$ = 0.01532 x (thickness in mm) x GTR.

These data presented on gas permeability show:

1.) Major differences in permeability among the membranes reflecting variation, in polymer type, compound composition, and thickness.

2.) Permeability of polymeric liner materials can differ for a given generic polymer type due to compound variation, (e.g. filler and plasticizer contents).

3.) Permeability of a membrane can differ greatly with the gas.

4.) Gas transmission of a membrane decreases with increased thickness.

Table IV — Permeability of Polymeric Membrane Liners to Gases at 23°C, Determined in Accordance With ASTM D1434, Procedure V.

Liner description				Gas transmission rate (GTR), mL (STP)/m²·d·atm			Gas permeability coefficient (P), barrer		
Polymer	Liner serial number[a]	Thickness, mm	Compound type[b]	CO_2	CH_4	N_2	CO_2	CH_4	N_2
Butyl	44	1.60	XL	512	120	19.7	12.5	2.92	0.480
CPE	77	0.72	TP	106[c]	6.31[c]	1.45[c]	1.16[c]	0.069[c]	0.016[c]
CSPE	6R	0.82	TP	122	21.6	26.2	1.52	0.270	0.33
CSPE	55	0.86	TP	418	124	27.1	5.47	1.62	0.36
ELPO	36	0.58	CX	1450	280	125	12.8	2.47	1.10
EPDM	83R	0.89	TP	2720[d]	...	...	36.8[d]	...	...
EPDM	91	0.90	XL	5260	1400	314	72.0	19.2	4.30
EPDM	8	1.50	XL	...	470[e]	...	...	10.7[e]	...
Neoprene	90	0.90	XL	716	80.9	31.1	9.81	1.11	0.43
PB	221	0.71	CX	818	248	62.3	8.84	2.68	0.67
HDPE	265	0.61	CX	729	138	...	6.77	1.28	...
HDPE	269	0.86	CX	467	104	...	6.11	1.36	...
LDPE	21	0.25	CX	6180[d]	1340[d]	...	23.5[d]	5.10[d]	...
LLDPE	281	0.46	CX	1370	322	...	9.59	2.25	...
PVC	93	0.25	TP	7730[d]	1150[d]	...	29.4	4.38[d]	...
PVC	88	0.49	TP	3010	446	108	22.4	3.32	0.81
PVC	59	0.81	TP	2840[d]	285[d]	...	35.0[d]	3.51[d]	...

[a]STP = Standard temperature and pressure.
[b]One barrer = 10^{-10} mL (STP)·cm/cm²·s·cm Hg.
[c]Matrecon liner serial number; R = Fabric-reinforced.
[d]XL = Crosslinked; TP = Thermoplastic; CX = Partially crystalline.
[e]Measured at a pressure gradient of 40 psi; all others measured at 20 psi.
[f]Measured at 30°C.
[g]Measured at 20°C.

5.) Higher polymer crystallinity yields lower permeability, as shown when comparing LDPE, LLDPE (linear low-density polyethylene), and HDPE.

6.) Permeability of polymeric membranes to gases increases with temperature in accordance with Arrhenius equation.

The permeability of polymeric membranes to water vapor is important to a variety of applications such as the covers for reservoirs and other impoundments, the lining of canals and tunnels, and as a moisture barrier in various buildings and structures.

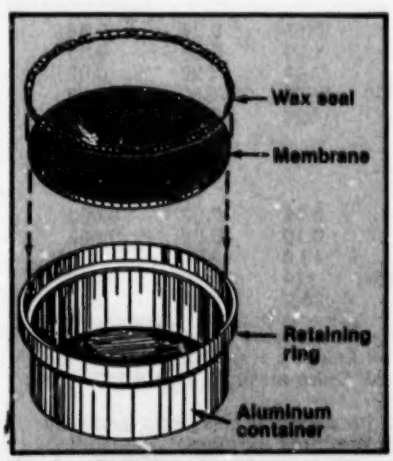

Fig. 3 — Exploded view of water vapor transmission cup used in ASTM E96 (2).

The WVT rates of polymeric membrane liners were determined by ASTM E96, Procedure BW(2). In this procedure, a circular specimen of the liner is sealed with molten wax into the mouth of an aluminum cup partially filled with deionized water. The test cell is illustrated in Fig. 3. The entire assembly is kept in an inverted position so that water is in contact with the membrane surface, and stored in a cabinet maintained at 23°C and a relative humidity (RH) of 50±5% and equipped with a small fan to ensure uniform air velocity over the surfaces of the specimens as required by the procedure. The WVT occurs across a water vapor pressure gradient of 100% RH (inside the cup) to 50% RH.

The test cells are periodically weighed and the resulting data are reduced using a linear regression program to yield a loss rate which can be converted to a WVT value in units of g/m²·d. Transmission of one g/m²·d of water is equal in practical units to 1.07 gallon per acre per day.

The water vapor transmission (WVT) rate of a membrane is the time rate of water vapor flow normal to its surfaces under steady conditions through a unit area under the conditions of test. The unit for WVT used in this report is 1 g

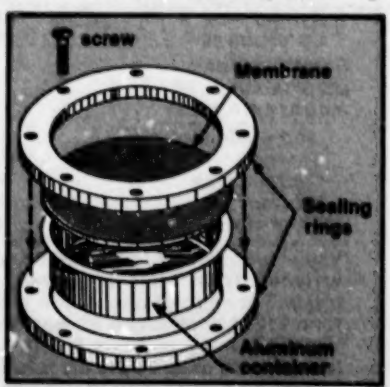

Fig. 4 — Exploded view of SVT cup with aluminum sealing rings.

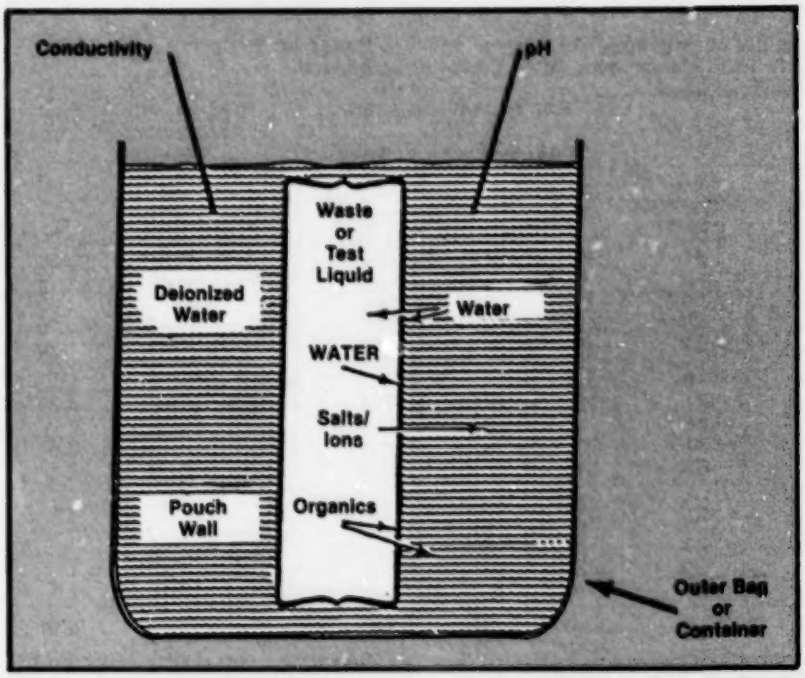

Fig. 5 — Pouch assembly with an aqueous waste or test liquid to show the movement of waste constituents during the pouch test. The filled pouch is immersed in deionized water. Arrows indicate the flow of specific constituents.

per square meter per day. The water vapor permeance of the material is the ratio of its WVT to the vapor pressure gradient across the two surfaces. The unit of permeance used is a metric perm, or 1 g per square meter per day per mm of mercury. The permeance value of a sheet if a rational basis for evaluating its performance and comparing various membranes for a given application. The water vapor permeability of a homogenous membrane is a property of the composition which may vary with exposure conditions. The permeability of a membrane is the product of its permeance and its thickness. The unit used in this report is the metric perm-centimeter or 1 g per square meter per day per mm Hg per centimeter thickness (ASTM E96).

As with the gas permeability data, permeability to water vapor varies considerably among the polymer types; for example, the rates

Table V — Permeability of Polymeric Membrane Liners to Various Solvents; Measured According to ASTM E96 Modified to Test Solvents.

Polymer	CSPE	ELPO	HDPE		HDPE-A			LDPE	PD	Teflon
Liner number	170R	172	184	179	180	181	182	108	221	234
Thickness, mm	1.07-1.12	0.53-0.61	0.77-0.83	2.42-2.81	0.53	0.85-0.88	0.97	0.74-0.76	0.64-0.74	0.10
Type of compound	TP	CX	CX	CX	CX	CX	CX	CX	CX	CX
Solvent vapor transmission (SVT), g/m²·d										
Methyl alcohol	...	2.10	0.16	...	...	0.50	...	0.74	0.35	0.34
Acetone	221	8.62	0.56	...	...	2.19	...	2.83	1.23	1.27
Cyclohexane	...	7.60	11.7	...	...	151	...	161	616	0.026
Xylene	...	359	21.6	6.86	295	212	220	116	178	0.16
Chloroform	...	3230	54.8	15.8	...	506	...	570	2120	20.6
Solvent vapor permeance[a], 10^{-4} metric perms (SVT/mm Hg)										
Methyl alcohol	...	1.88	0.14	...	...	0.45	...	0.66	0.31	0.30
Acetone	104	4.07	0.26	...	...	1.03	...	1.33	0.58	0.60
Cyclohexane	...	854	13.1	...	...	170	...	181	692	0.03
Xylene[b]	...	5120	308	87.9	4210	3020	3140	1650	2540	2.28
Chloroform	...	1810	30.8	8.88	...	284	...	320	2.28	11.6
Solvent vapor permeability[c], 10^{-4} metric perms·cm										
Methyl alcohol	...	0.11	0.01	...	...	0.04	...	0.05	0.02	0.003
Acetone	11.4	0.23	0.02	...	...	0.09	...	0.10	0.04	0.006
Cyclohexane	...	48.7	1.05	...	...	14.7	...	13.6	47.8	2.9×10^{-4}
Xylene[b]	...	292	24.6	25.6	223	262	304	124	175	0.002
Chloroform	...	103	2.46	2.32	...	24.6	...	24.0	82.2	0.12

[a]Vapor pressure of the solvents for permeance calculations was calculated by the Antoine equation using the variables from Table 10-8, Vapor Pressure of Various Organic Compounds in Lange's Handbook of Chemistry(3). The vapor pressures in mm of Hg at a standard room temperature of 23°C are methyl alcohol 112, acetone 212, cyclohexane 89, and chloroform 178.
[b]Vapor pressure of 7 mm of Hg, which is the average of the individual values for o-xylene, m-xylene, and p-xylene(3), was used in the calculations since the solvent used was a mixture of the three isomers.
[c]The median thickness value was used to calculate the permeability.

are much lower through hydrocarbon types (e.g. butyl rubber, EPDM, ELPO) than through polar types (e.g. ECO and nitrile rubber). Also, within a polymer type there is considerable variation due to differences in composition. Increased thickness and increased crystallinity, in the case of crystalline materials, reduce permeability rates.

Solvent Vapor Transmission

Considerable data*(9, 10)* exist with respect to the transport of organics through polymeric films, but almost no data exist with respect to polymeric membrane liners. Preliminary experiments were performed on neat solvents to assess their transmission rates under controlled conditions through different membranes. solvent vapor transmission rates were determined by a modification of ASTM E96 in which a circular specimen of the liner is mechanically clamped onto the mouth of an aluminum cup partially filled with the test solvent (Fig. 4). The method differs from E96, Procedure BW, in that the cups are stored in an upright position so that solvent vapor contacts the membrane. SVI occurs as a result of the concentration gradient across the membrane by the presence of a saturated atmosphere within the cup and the essentially zero level outside the cup. The rate of SVI is determined as described above for WVT.

SVT data for a series of membranes selected for good solvent resistance are given in Table V. Also present in Table V are the values for solvent vapor permeance and solvent vapor permeability calculated from solvent vapor transmission and the vapor pressure at 23°C of the respective solvents and the thickness of the respective membranes. These data are for five organic solvents, i.e. methanol, acetone, cyclohexane, xylene, and chloroform. Although limited, the data show substantially different transmission rates among the membranes and among the different solvents. Increased crystallinity among the polyethylene membranes reduces transmission, as does increased thickness. The alloying of HDPE results in significantly higher transmission and permeability.

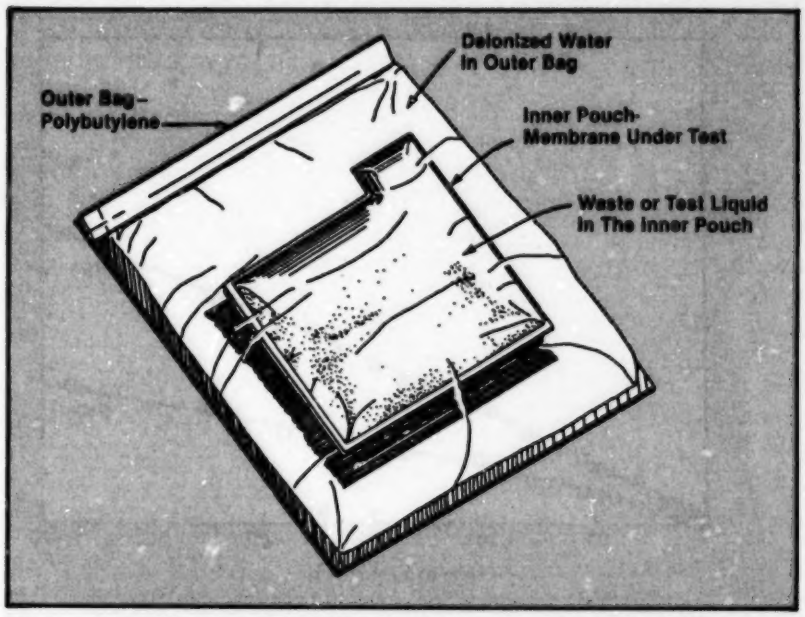

Fig. 6 — Schematic of pouch assembly showing inner pouch made of membrane material under test. The pouch is filled with waste liquid and sealed at the neck. The outer polybutylene bag, which can be easily opened, is filled with deionized water. For this configuration the water in the outer bag is monitored for pH, conductivity, and odor; the pouch is monitored for weight change.

Permeability of Membranes in Pouch Tests

The permeabiliity characteristics of thermoplastic and partially crystalline polymeric membranes have been studied in a pouch procedure which simulates some in-service conditions of liners in waste disposal facilities*(4, 6, 7, 8)*. In this procedure, small containers are fabricated of the membrane (Fig. 5 and 6) to be tested and filled with a test liquid, sealed, and immersed in a liquid of known composition. When the outer liquid initially is DI water, permeabilities of the membrane to water and to the dissolved constituents can be determined by observing the changes with time in the weight of the pouch and changes in the pH, electrical conductivity, and the composition of

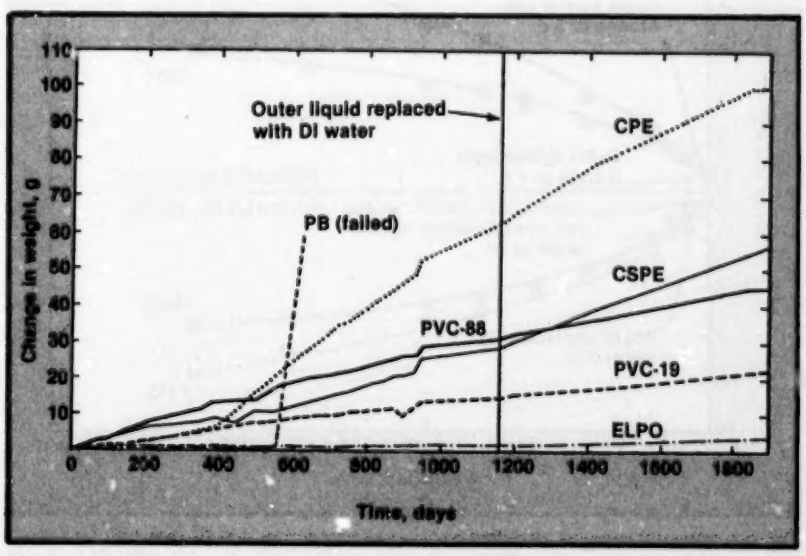

Fig. 7 — Weight changes of pouches containing a highly acidic waste.

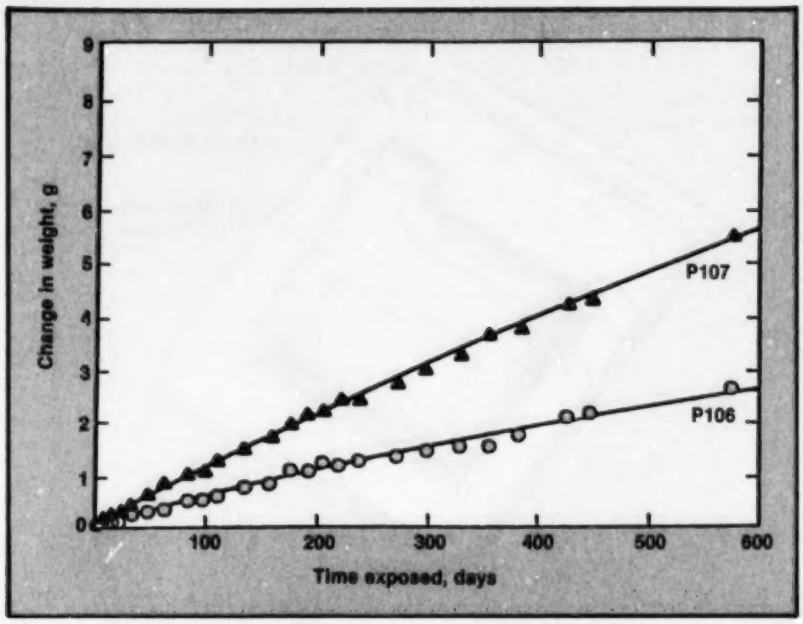

Fig. 8 — Weight changes of PVC pouches containing 5% (P106) and 10% (P107) aqueous solutions of LiC1 during immerion in DI water.

the outer water. Because of differences in the concentrations of different molecular species across the membrane wall, osmosis will cause the outer water to enter the pouch and cause ions and dissolved constituents in the pouch liquid to tend to leave the pouch and enter the outer water. An increase in weight of the pouch may only reflect absorption of the outer water by the wall and not permeation of water into the pouch. When the test is completed the pouch and its contents are weighed separately to determine the actual amounts that have been absorbed by the wall and the amounts that have permeated the pouch wall.

Experimental Results. The studies of the permeability of polymeric liners using the pouch procedure included membranes of CPE, CSPE, HDPE, HDPE-A, LDPE, PB, PVC, and PVC-OR*(6)*. The test liquids included aqueous salt solutions (of sodium chloride and of lithium chloride), organic solvents (acetone and xylene), mixtures of acetone and water, water-soluble and organic-soluble dyes, and several actual waste liquids.

Permeability to Water. Of nine pouches filled with the 5% NaC1 aqueous solution, eight showed the transmission of water into the pouch, as judged by the increased weight of the pouch contents. The ninth pouch, CSPE 55, gained in weight but showed a weight loss for its contents indicating absorption of the pouch liquid by the wall. The pouches with a highly acidic waste showed the transmission of water from outside to inside the pouches. The weight changes during exposure are shown in Fig. 7. The results indicate that ELPO has a low permeability. The behavior of pouches containing a highly alkaline waste was similar except for the ELPO pouch which gained weight after 300 days of exposure, indicating a slowly developing effect of the waste on this membrane.

The effect of the concentration gradient across the pouch wall is clearly demonstrated in the PVC pouches with LiC1 (Figure 8). The pouches containing 5% LiC1 show a rate of transmission that is approximately half that of the pouches with 10% LiC1.

The pouches filled with acetone or xylene and placed in DI water showed the movement of each solvent out of the pouches and no water movement into the pouches (Figs. 9 and 10). The pouches with 50:50 acetone: DI water showed outward movement of acetone when immersed in DI water and inward movement of acetone when immersed in acetone.

Permeability to Ions. In the experiments performed with salt solutions, the ions showed little tendency to permeate polymeric sheetings. Even at high concentration

(concludes on page 66.)

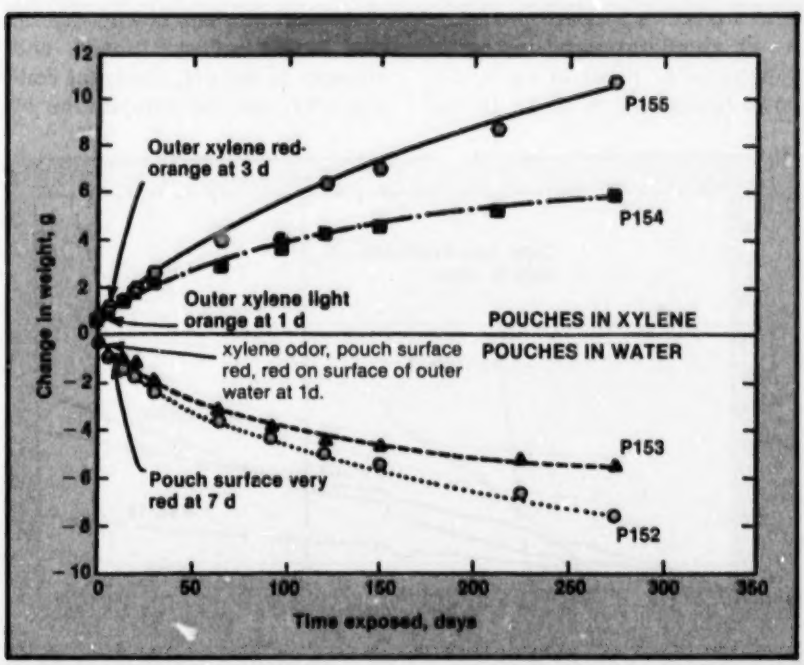
Change in weight, g
Time exposed, days
P155
P154
P153
P152
Outer xylene red-orange at 3 d
Outer xylene light orange at 1 d
POUCHES IN XYLENE
POUCHES IN WATER
xylene odor, pouch surface red, red on surface of outer water at 1d.
Pouch surface very red at 7 d

Fig. 9 — Weight changes in HDPE-A pouches filled with xylene and 1% Automate Red.

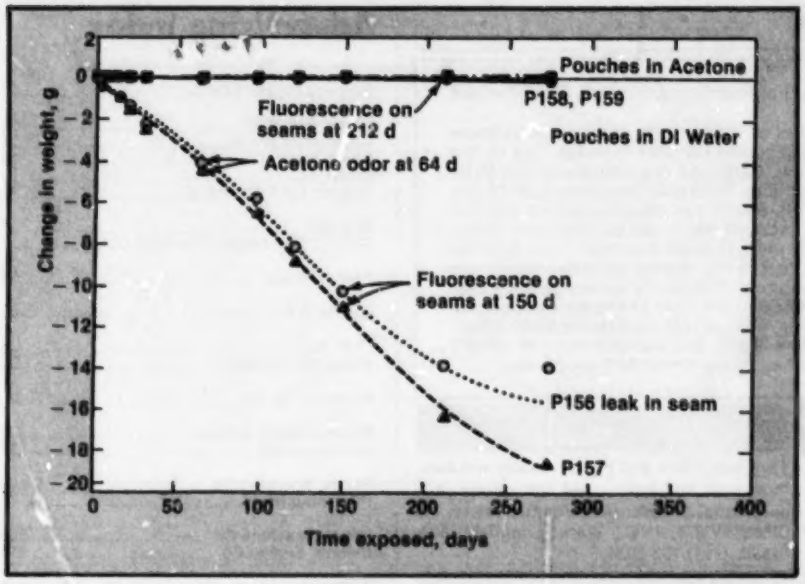

Fig. 10 — Weight changes in HDPE-A pouches filled with acetone and 1% Fluorescent Yellow.

(continued from page 66.)

gradients (10% LiCl solution), the electrical conductivity of the outer liquids remained low. In the tests with the highly acidic waste, the hydrogen ions in the pouches appeared to have migrated through the walls; the pH of the outer solution dropped and the electrical conductivity increased.

Permeability to Organic Dyes. Three water-soluble and two organic soluble dyes were studied in pouch experiments at 1% concentrations. The water-soluble types included sodium fluorescein, Sevron Red, and methyl violet. The sodium fluorescein showed positive transmission through PVC-OR, and trace transmission through HDPE, PB, and PVC. Sevron Red in water showed no detectable transmission through HDPE-A and PB. Methyl violet in the 50:50 acetone:water mixture showed no detectable transmission through HDPE-A. In contrast to the water-soluble dyes, the two organic-soluble dyes, Automate Red and Fluorescent Yellow, in pouches containing acetone and xylene quickly permeated the HDPE-A pouch walls (Fig. 9).

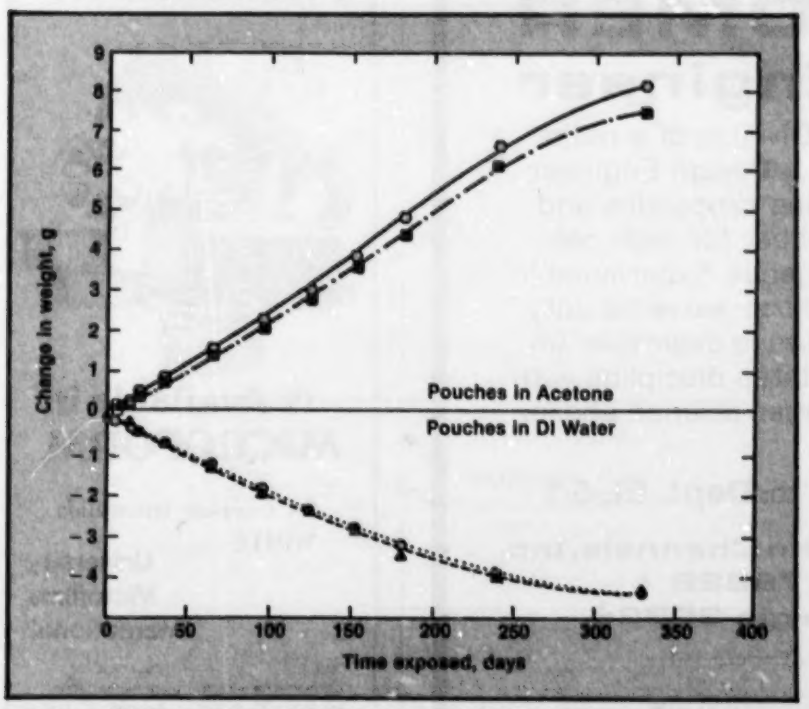

Fig. 11 — Weight changes in pouches of 20 mil HDPE-A (180) filled with 50:50 acetone: DI water and 1% methyl violet immersed in acetone and in DI water.

ACKNOWLEDGMENTS

The major portion of the work reported in this paper was performed under Contract 68-03-2134, "Evaluation of Liner Materials Exposed to Leachate," Contract 68-03-2173, "Evaluation of Liner Materials Exposed to Hazardous and Toxic Wastes," and Contract 68-03-2969, "Long-term Testing of Liner Materials," with the Municipal Environmental Research Laboratory of the U.S. Environmental Protection Agency.

REFERENCES

(1) ASTM D1434, *Test Methods for Gas Transmission Rates of Plastic Film* and Sheeting, American Society for Testing and Materials, (Philadelphia, 1975).

(2) ASTM E96, *Test Methods for Water Vapor Transmission of Materials,* American Society for Testing and Materials, (Philadelphia, 1980).

(3) Dean, J. A. "Lange's Handbook of Chemistry," 12th Edition. McGraw-Hill Book Co. (1979).

(4) Haxo, H. E., Haxo, R. S., Nelson, N. A., Haxo, P. D., White, R. M., and Dakessian, S., *Final Report: Liner Materials Exposed to Hazardous and Toxic Sludges,* U.S. Environmental Protection Agency, (Cincinnati, Ohio).

(5) Haxo, H. E., J. A. Miedema, and N. A. Nelson. *Permeability of Polymeric-Membrane Lining Materials,* In: "Proceedings of the International Conference on Geomembranes," Denver, Colo. Vol. 1. Sponsored by Industrial Fabrics Association International, St. Paul, Minn. pp. 151-156, 1984.

(6) Haxo, H. E. and Nelson, N. A., *Permeability Characteristics of Flexible Membrane Liners Measured in Pouch Tests,* in "Proceedings of the 10th Annual EPA Research Symposium," U.S. Environmental Protection Agency, (Cincinnati, Ohio).

(7) Haxo, H. E., White, R. M., Haxo, P. D., and Fong, M. A., *Final Report: Evaluation of Liner Materials Exposed to Municipal Solid Waste Leachate,* NTIS No. PB 83-147-801, U.S. Environmental Protection Agency, (Cincinnati, Ohio, 1982).

(8) Matrecon, Inc., *Lining of Waste Impoundment and Disposal Facilities.* SW-870 Revised. U.S. Environmental Protection Agency, (Washington, D.C., 1983), 448 pp. GPO #055-00000231-2.

(9) Yasuda, H., "Permeability Constants," in *Polymer Handbook,* Interscience (New York, 1966).

(10) Yasuda, H., Clark, H. G. and Stannett, V., "Permeability," in *Encyclopedia of Polymer Science & Technology,* Vol. 9, Interscience, (New York, 1968).

Presented at the Education Symposium, Migration of Gases, Liquids, and Solids in Elastomers at the 126th Meeting of the Rubber Division, American Chemical Society, Denver, Colo., Oct. 23, 1984.